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**EMULSION-BASED CONTROL OF ELECTROSPUN FIBER MORPHOLOGY****CROSS-REFERENCE TO RELATED APPLICATIONS**

This application claims the benefit of provisional Application No. 60/556,637, filed on  
5 March 25, 2004, which is incorporated herein in its entirety.

**STATEMENT REGARDING FEDERALLY  
SPONSORED RESEARCH OR DEVELOPMENT**

This research was supported in part by U.S. Government funds (National Institute of  
10 Health, grant number R24-AI47739-03), and the U.S. Government may therefore have certain  
rights in the invention.

**SPECIFICATION****BACKGROUND OF THE INVENTION****1. FIELD OF INVENTION**

15 This invention relates to a process of making a fiber and more particularly to ways of  
modifying the fiber's morphology.

**2. DESCRIPTION OF RELATED ART**

Electrospinning (ES) is an atomization process of a conducting fluid which exploits the  
interactions between an electrostatic field and the conducting fluid. During electrospinning,  
20 fibers with micron or sub-micron sized diameters are extruded by means of an electrostatic  
potential from a polymer solution (see U.S. Patent No. 1,975,504 to Formhals). When an external  
electrostatic field is applied to a conducting fluid (e.g., a semi-dilute polymer solution or a  
polymer melt), a suspended conical droplet is formed, whereby the surface tension of the droplet  
is in equilibrium with the electric field. Electrostatic atomization occurs when the electrostatic  
25 field is strong enough to overcome the surface tension of the liquid. The liquid droplet then  
becomes unstable and a tiny jet is ejected from the surface of the droplet. As it reaches a  
grounded target, the material can be collected as an interconnected web containing relatively fine,  
i.e. small diameter, fibers. The resulting films (or membranes) from these small diameter fibers  
have very large surface area to volume ratios and small pore sizes. This process typically yields  
30 non-woven mats or felts composed of round fibers that are extremely pliable. Due to their high-  
surface area and good mechanical characteristics, electrospun meshes have traditionally found  
applications in filtration and composite reinforcement. For the very same reasons, felts and  
meshes derived from biocompatible polymers such as poly(lactic acid) and its copolymer with  
glycolic acid and other polyesters are being explored as substrates (scaffolds) for association of

cells in the engineering of tissue (see Kenawy et al., *Biomaterials*, 2003, 24(6), 907 describing making a fiber by electrospinning process from a single-phase system containing ethylene vinyl alcohol, 70% propanol and 30% water). Such pliable porous media is particularly suited for engineering of skin, vascular and neural prostheses.

5 Electrospun materials possess a high aspect ratio to allow for cell attachment and spreading, which is a desired property for tissue engineering (TE) applications. The longest axis of a spread cell is typically around 5-10 micrometers. ES process is not amenable to significant modifications. Parameters that can be varied in the ES process are the electric field, the distance between the "Taylor Cone" and the target, and polymer solution viscosity (Fridrikh et al., G.C. 10 *Phys Rev Lett.* 2003, 90(14), 144502). Due to the complexity of the fiber forming process, very few attempts have been made to alter geometry of electrospun fibers. Recently, Reneker and co-workers have observed the formation of branched and ribbon-like fibers in some solvent systems and have attributed this to the collapse of a polymer skin due to buckling instability similar to that seen in garden hoses (see Koombhongse et al., *Polym. Sci.: Part B: Polym. Phys.* 2001, 39, 15 2598–2606). However, the formation of such fibers is not achievable in a predictable manner under generally known ES operating conditions.

U.S. Patent No. 4,323,525 to Bornat is directed to a process for the production of tubular products by electrostatically spinning a liquid containing a fiber-forming material. The process involves introducing the liquid into an electric field through a nozzle, under conditions to 20 produce fibers from a fiber-forming material, which tends to be drawn to a charged collector, and collecting the fibers on a charged tubular collector, which rotates about its longitudinal axis to form a fibrous tubular product. However, there is no suggestion or teaching of how to control the physical characteristics of the tubular product, other than by controlling the charge and rotation speed of the tubular collector. The spinning process of the '525 patent is used to 25 fabricate tubular products having a homogenous fiber matrix across the wall thickness.

U.S. Patent No. 4,689,186 to Bornat is directed to a process for making polyurethane tubular products by electrostatically spinning a fiber-forming solution containing polyurethane. The electrospinning process of the '186 patent is used to fabricate tubular products having a homogenous fiber matrix.

30 Sanders et al. describe entrapment of water droplets in polyvinyl acetate fibers spun from a suspension containing a polymer in methylene chloride and protein (BSA) in a phosphate buffer. The fiber-forming composition was a cloudy suspension and not an emulsion. The ratio

of organic solvent to water is 40:1 or about 2.4 vol%. There was no emulsifying agent used in the fiber-forming composition (see *Macromolecules* 2003, 36, 3803-3805).

There are methods other than electrospinning for creation nanofibers. For example, U.S. Patent No. 6,520,425 to Reneker describes forming nanofibers by using a pressurized gas stream to overcome problems associated with liquids having higher viscosities and inability to create higher forces than electric fields can supply.

Despite the foregoing development, it is desired to provide a method of making fibers with desirable morphology in a predictable and controllable manner.

All references cited herein are incorporated herein by reference in their entireties.

#### BRIEF SUMMARY OF THE INVENTION

Inventors have discovered that fiber morphology can be controlled by using multiphasic compositions, such as, for example, a water/oil emulsion or a double emulsion as a fiber-forming medium. The present invention provides a method of making a fiber comprising providing a first component including water, wherein the first component has a first evaporation rate, providing a second component including a polymer dissolved in a solvent, wherein the second component has a second evaporation rate, provided that the second evaporation rate is higher than the first evaporation rate, combining the first component and the second component to make an emulsion, applying a force to the emulsion, and extruding the emulsion to make the fiber, wherein the fiber has an outer surface, an internal cavity and an outer diameter of at most 10 micrometers.

Also provided is a fiber manufactured by the method of the invention.

Further provided is a fiber made from the emulsion comprising water, poly(lactic acid), and optionally a nanoparticle comprising silicone oxide and a biomolecule. In certain embodiments, the diameter of the fiber is from about 3 nm to 10 micrometers.

Also the invention provides an improvement to the known methods of making a fiber by electrospinning, wherein a fiber is formed by extruding a fiber-forming medium, such as a polymeric composition, from a vessel through an orifice under the influence of a force. In the improvement, the fiber-forming medium comprises an emulsion comprising (1) a first component comprising water, said first component is provided in an amount of at most 20 vol. %, and (2) a second component comprising a polymer, said second component is provided in an amount of at least 80 vol. %, on a condition that the first component has a first evaporation rate and the second component has a second evaporation rate and wherein the second evaporation rate is higher than the first evaporation rate.

## BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

The invention will be described in conjunction with the following drawings in which like reference numerals designate like elements and wherein:

Fig. 1 is a graph illustrating poly(lactic acid) (PLA) fiber diameter and morphology as a function of volume fraction of aqueous phase in a water/oil (W/O) emulsion.

Fig. 2 is an electronic microscope image of PLA fibers obtained by spinning from a single-phase system composed of PLA, chloroform and 1-methyl-2-pyrrolidinone (NMP).

Fig. 3 is an electronic microscope image of PLA fibers obtained by spinning from a W/O emulsion composed of 2.5 v/v % aqueous phase; the porous nature of the fibers is shown in the inset on the bottom left.

Fig. 4 is an electronic microscope image of PLA fibers obtained by spinning from a W/O emulsion composed of 14 v/v % aqueous phase.

Fig. 5 is an electronic microscope image of PLA fibers obtained by spinning from a W/O emulsion composed of 885  $\mu$ l PLA, 27  $\mu$ l NMP, 0  $\mu$ l PVA(10%) and 100  $\mu$ l colloid (sample E4).

Fig. 6 is an electronic microscope image of PLA fibers obtained by spinning from a W/O emulsion composed of 835  $\mu$ l PLA, 25  $\mu$ l NMP, 50  $\mu$ l PVA, and 100  $\mu$ l Colloid/Water (sample E2).

Fig. 7 is an electronic microscope image of PLA fibers obtained by spinning from a W/O emulsion composed of 835  $\mu$ l PLA, 25  $\mu$ l NMP, 50  $\mu$ l PVA, and 100  $\mu$ l Colloid/Water (sample E2).

Fig. 8 is an electronic microscope image of PLA fibers obtained by spinning from a W/O emulsion composed of 980  $\mu$ l PLA, 80  $\mu$ l NMP, 2.5  $\mu$ l PVA and 2.5  $\mu$ l Colloid/Water (sample WC4).

Fig. 9 is an electronic microscope image of PLA fibers obtained by spinning from a W/O emulsion composed of 1 g of Alginate Beads suspended in about 2 ml E4 sample and 125  $\mu$ l Colloid/Water (sample AB8).

Fig. 10 is an electronic microscope image of PLA fibers obtained by spinning from a W/O emulsion composed of 1 g of Alginate Beads suspended in about 2 ml E4 sample and 125  $\mu$ l Colloid/Water (sample AB8).

## DETAILED DESCRIPTION OF THE INVENTION

Inventors have discovered that that fiber morphology can be varied by spinning from a multiphasic fiber-forming medium such as, for example, an emulsion, rather than from a solution or a dispersion. Advantageously, by using at least two-solvent systems having varying evaporation rates and miscibility, morphology of the resulting fiber can be controlled, wherein a preferential evaporation of the more volatile solvent causes the formation of outer surfaces or skins similar to those produced in, for example, a sausage casing process, where the less volatile liquid phase is entrapped and surrounded by a solidified polymer skin. Thus, the invention provides a method for making fibers of different morphologies, including, for example, flattened and porous forms. The ability to control morphology of the fiber is useful in various medical application such as, for example, tissue engineering, drug delivery, as well as non-medical application such as, for example, electronics. Another unexpected benefit of this invention is that due to the addition of aqueous phase, resulting fibers can be produced with smaller diameters, as compared to the fibers produced from a single-phase solution of identical polymer concentration.

Accordingly, the present invention provides a method of making a fiber from an emulsion comprising a first component including water, and a second component including a polymer dissolved in a solvent. In the method, a force is applied to the emulsion to extrude and separate the emulsion into a fiber, wherein the fiber has an outer surface, an internal cavity and an outer diameter of at most 10 micrometers. The force is preferably created by an electrostatic field, i.e., an electric force. In this example, the emulsion is preferably electrically conductive or includes electrically conductive materials. Other examples of the force include a magnetic force and an electromagnetic force. Another non-limiting example of the force is a force of pressurized gas.

Apparatuses useful in this invention for creation of the electrostatic field are known in the art such as, for example, electrosp spinners described by Fridrikh et al. and Bornat supra. The technique of spinning liquids has been described in the art, for example, in U.S. Patent No. 4,044,404. These apparatuses employ the electric force for spinning the multiphasic fiber-forming medium of the invention. Another type of apparatuses employs a compressed gas as described by U. S. Patent No. 6,520,425 by Reneker.

The multiphasic fiber-forming medium of the invention is an emulsion, such as, for example, a water/oil emulsion, a double emulsion or an emulsion in which particles are dispersed. In forming the emulsion, at least two components are mixed, wherein the first component (an aqueous phase or a hydrophilic component) has a first evaporation rate, and the

second component (an oil phase or a lipophilic component) has a second evaporation rate, such that the second evaporation rate is higher than the first evaporation rate.

By varying the ratio of components in the emulsion, desired morphology can be achieved as described below. In certain embodiments, the first component and the second component are provided at a ratio, wherein the ratio is adapted to change morphology of the fiber and its diameter. Examples of fibers with various morphologies include flat fiber, round fiber, porous fiber and combinations thereof (see Figs. 2-9). It was observed for an exemplary PLA emulsion, the transition from round to porous fibers occurs in the range of 2-5% volume fraction of aqueous phase in the emulsion. Above 5% volume fraction of aqueous phase, fibers with a flat-ribbon morphology are obtained.

In certain embodiments, the first component comprises water and optionally, glycerol and poly(vinyl alcohol). In certain embodiments, the first component comprises at most 20 vol. % of the emulsion. In certain embodiments, the first component comprises from about 5 to about 20 vol. %. In certain embodiments, the first component comprises from about 2 to 5 vol. %.

In certain embodiments, the second component comprises at least 80% of the emulsion. In certain embodiments, the second component comprises polymer, preferably dissolved in an organic solvent. Non-limiting examples of suitable polymers include poly(styrene), poly(urethane), poly(lactic acid), poly(glycolic acid), poly(ester), poly(alpha-hydroxy acid), poly(epsilon-caprolactone), poly(dioxanone), poly(orthoester), poly(ether-ester), poly(lactone), poly(carbonate), poly(phosphazene), poly(phosphanate), poly(ether), poly(anhydride), mixtures thereof and copolymers thereof.

In certain embodiments, the organic solvent is a member selected from the group consisting of methylene chloride, chloroform, ether, hexane, pentane, petroleum ether, cresol, dichloroethane, ethyl acetate, methyl ethyl ketone, dioxane, propylene carbonate, and butyl acetate.

Various additives can be added to the emulsion, such as, for example, a surfactant, an emulsifier, and a stabilizer for impacting properties of emulsion such as stability, consistency, etc. Depending on ratios of first component to the second component, the emulsion can be a microemulsion.

In certain embodiments, the emulsion comprises a third component such as, for example, a biomolecule, a cell, a particle, and a gel. The third component can be dissolved in either or both of the phases or it can be dispersed. Depending on the choice of the phase, the third component can be located inside or outside of the fiber. For example, if the third component is

dissolved in the aqueous phase, upon forming of the fiber, it will be trapped inside, upon evaporation of the solvent of the second phase. Also, if the third component is dissolved in the second phase, upon forming of the fiber, it will be trapped in the outer skin of the fiber.

Non-limiting examples of suitable biomolecules include a bioactive polypeptide, a polynucleotide coding for the bioactive polypeptide, a cell regulatory small molecule, a peptide, a protein, an oligonucleotide, a nucleic acid, a poly(saccharide), an adenoviral vector, a gene transfection vector, a drug, and a drug delivering agent.

Non-limiting examples of suitable cells include chondroblast, chondrocyte, fibroblast, an endothelial cell, osteoblast, osteocyte, an epithelial cell, an epidermal cell, a mesenchymal cell, a hemopoietic cell, an embryoid body, a stem cell, and dorsal root ganglia.

In certain embodiments, the particle is a colloidal particle or a solid particle. Patterning the surfaces of fibers with particles has practical applications, for example, in tissue engineering where presentation of chemical and physical cues on degradable scaffolds allows a more precise control over cell-scaffold interactions.

In certain embodiments, the colloidal particle has a diameter of from about 3nm to about 10 micrometers and includes a polymer, an oxide, a nitride, a carbide, calcium silicate, calcium phosphate, calcium carbonate, a carbonaceous material, a metal, and a semiconductor.

In certain embodiments, the solid particle has a diameter of about 3nm to about 10 micrometers and said solid nanoparticle is a member selected from the group consisting of a polymer, an oxide, a nitride, a carbide, calcium silicate, calcium phosphate, calcium carbonate, a carbonaceous material, a metal, and a semiconductor.

An example of incorporation of solid particles is encapsulation silica nanoparticles (SNP) within polymeric fibers. The presence of SNP within the fibers was verified using SEM and BET measurements, which revealed the presence of a phase with a very high surface area ( $> 50 \text{ m}^2/\text{gm}$ ). Also, carbon nanotubes and magnetic particles are examples of solid particles suitable in this invention.

Non-limiting examples of surfactants include non-ionic surfactants such as, for example, PLURONIC, polyvinyl alcohol, poly(sorbate) (such as, for example, TWEEN-80 and SPAN-20), oleyl alcohol, glycerol ester, sorbitol, and carboxy methoxy cellulose or an ionic surfactant such as, for example, sodium dodecyl sulfonate, sodium dodecyl benzene sulfonate, oleic acid, albumin, ova-albumin, lecithin, natural lipids, and synthetic lipids.

In certain embodiments, the emulsion comprises water mixed with poly(vinyl alcohol) as the first components and poly(lactic acid) dissolved in organic solvent as the second component,

and optionally, silicone oxide nanoparticle having a biomolecule attached to the nanoparticle's surface as the third component.

The invention also provides a fiber manufactured by the method of the invention as described above, wherein the morphology of the fiber is controlled by varying a ratio of the first component to the second component.

A non-limiting example of the desired fiber is a fiber made from the emulsion comprising water, poly(lactic acid), and optionally a nanoparticle comprising silicone oxide and a biomolecule. In certain embodiments, the diameter of the fiber is from about 3 nm to 10 micrometers.

Also the invention provides an improvement to the known methods of making a fiber by electrospinning, wherein a fiber is formed by extruding a fiber-forming medium, such as a polymeric composition, from a vessel through an orifice under the influence of a force. In the improvement, the fiber-forming medium comprises an emulsion comprising (1) a first component comprising water, said first component is provided in an amount of at most 20 vol. %, and (2) a second component comprising a polymer, said second component is provided in an amount of at least 80 vol. %, on a condition that the first component has a first evaporation rate and the second component has a second evaporation rate and wherein the second evaporation rate is higher than the first evaporation rate.

The invention will be illustrated in more detail with reference to the following Examples, but it should be understood that the present invention is not deemed to be limited thereto.

#### EXAMPLE

As a non-limiting example, the invention will be described based on the effect of a water/oil emulsion on the morphology of poly(L-lactic acid) (PLA) fibers obtained by ES.

Materials: Poly(L-lactic acid) (MW=300,000) (PLA) was purchased from Polysciences, Inc. (Warrington, PA). Poly(vinyl alcohol) (MW=10,000, 85% hydrolyzed) (PVA) and 1-methyl-2-pyrrolidinone (99.5%) (NMP) were purchased from Aldrich Chemical Co (Milwaukee, WI). Chloroform (HPLC grade, 99.8%) was purchased from Fisher Scientific (Pittsburgh, PA). Poly(acrylic acid) coated Silica colloids 500 nm in diameter were produced by a sol-gel process. All chemicals were used as received without further purification unless otherwise noted.

Preparation of Polymer Solutions. Water-in-oil (W/O) emulsion of PLA was prepared by emulsifying a 2% stock of PLA in chloroform with 5% PVA solution in water and a fixed volume of NMP (Table 1). NMP was added to the mixture to serve as a phase compatibilizer (NMP is soluble in both water and chloroform) and to retard the evaporation of chloroform (oil



phase). Formulations containing varying amounts of aqueous phase and PVA and PLA were studied and are shown in Table 1. To aid in the analysis of the evolution of fiber morphology and get an insight into the mechanism of fiber formation, silica colloids (< 1% v/v) were added to some of the formulations. All components were metered using an Eppendorf pipette, mixed by vortexing and sonicated for 45 seconds (20 KHz, Vibra Cell, Sonic Systems) to ensure full emulsification.

Table 1 Description of Composition of Samples

Sample	Composition	Sample	Composition
C1	990 $\mu$ l PLA 30 $\mu$ l NMP	V3	885 $\mu$ l PLA 27 $\mu$ l NMP 50 $\mu$ l PVA (0.5%) 50 $\mu$ l Colloid/Water
C2	885 $\mu$ l PLA 27 $\mu$ l NMP 50 $\mu$ l PVA 50 $\mu$ l Water	AB8	Alginate Beads suspended in ~ 2 ml of E4 solution 125 $\mu$ l Colloid/Water
C3	885 $\mu$ l Chloroform 27 $\mu$ l NMP 50 $\mu$ l PLA 50 $\mu$ l Water	WC1	935 $\mu$ l PLA 29 $\mu$ l NMP 25 $\mu$ l PVA 25 $\mu$ l Colloid/Water
E1	885 $\mu$ l PLA 27 $\mu$ l NMP 50 $\mu$ l PVA 50 $\mu$ l Colloid/Water	WC2	960 $\mu$ l PLA 29 $\mu$ l NMP 12.5 $\mu$ l PVA 12.5 Colloid/Water
E2	835 $\mu$ l PLA 25 $\mu$ l NMP 50 $\mu$ l PVA 100 $\mu$ l Colloid/Water	WC3	975 $\mu$ l PLA 30 $\mu$ l NMP 5 $\mu$ l PVA 5 $\mu$ l Colloid/Water
E3	905 $\mu$ l PLA 27 $\mu$ l NMP 50 $\mu$ l PVA 25 $\mu$ l Colloid/Water	WC4	980 $\mu$ l PLA 80 $\mu$ l NMP 2.5 $\mu$ l PVA 2.5 $\mu$ l Colloid/Water
E4	885 $\mu$ l PLA 27 $\mu$ l NMP 10 $\mu$ l PVA(10%) 100 $\mu$ l Colloid	WC5	485 $\mu$ l PLA 15 $\mu$ l NMP 250 $\mu$ l PVA 250 $\mu$ l Colloid/Water
EL4	885 $\mu$ l PLA 27 $\mu$ l NMP 10 $\mu$ l PVA(10%) 100 $\mu$ l Ludox Colloid	WC6	730 $\mu$ l PLA 23 $\mu$ l NMP 125 $\mu$ l PVA
V1	885 $\mu$ l PLA 27 $\mu$ l NMP	WC7	830 $\mu$ l PLA 26 $\mu$ l NMP

Sample	Composition	Sample	Composition
	50 $\mu$ l PVA (2.5%) 50 $\mu$ l Colloid/Water		75 $\mu$ l PVA 75 $\mu$ l Colloid/Water
V2	885 $\mu$ l PLA 27 $\mu$ l NMP 50 $\mu$ l PVA (1%) 50 $\mu$ l Colloid/Water	WC8	785 $\mu$ l PLA 24 $\mu$ l NMP 100 $\mu$ l PVA 100 $\mu$ l Colloid/Water

Electrospinning of PLA fibers. The polymer solution (typical volume 1 ml) was loaded into a 3 ml syringe fitted with a 16-gauge blunt tip needle. The syringe was mounted on a ring stand at a 45° angle below horizontal. The needle was connected to a high voltage power supply (Gamma High Voltage Research, Ormond Beach, FL). The counter electrode was connected to an aluminum foil (collecting target) placed at a distance of 15 cm away from the tip of the needle. The bias between each plate was then slowly increased until the eruption of the "Taylor Cone" and was then set at 25 kV. Fibers were collected on the aluminum foil until the solution was fully dispensed.

Electrospun fibers were imaged using a JEOL 6300FV field emission scanning electron microscope at an acceleration voltage of 10 KeV (see Figs. 2-9). Samples were mounted onto aluminum stubs using conductive carbon tape and then sputter coated with Pd-C to minimize charging. TIFF files of the images were then imported into Scion Image (NIH, Bethesda, MD) for analysis.

W/O emulsions of PLA dissolved in a chloroform/NMP mixture and water, stabilized by PVA, were used as a model two-phase system to study its effect on fiber morphology in the ES process. The choice of this system was driven by two considerations, namely, easy adaptability to biomedical applications and biocompatibility of the non-volatile components. Solutions containing up to 15% aqueous phase were successfully electrospun without any disruption of the fiber morphology. However, solutions that contained greater than 20% by volume of aqueous phase tended to spray as droplets suggesting the onset of instability of the "Taylor Cone". Inventors observed that by varying the volume fraction of the aqueous phase, the morphology and diameter of PLA fibers could be significantly impacted. In general, increasing the volume fraction of the aqueous phase yielded fibers with smaller diameters (Figure 1). One contributing factor could be the lower volume fraction of polymer at higher aqueous phase concentrations. Rheological effects are most likely the dominant component of the fiber-thinning process. However, inventors observed no correlation between PVA concentration and fiber diameter. A synergetic effect was observed, wherein an order of magnitude change in fiber diameter can be

achieved with the introduction of a small volume fraction of aqueous phase. The fiber diameter data can be fitted to an exponential decay process, which is consistent with a trend one may observe with respect to the stability of emulsions. The typical fiber morphology obtained in the ES process is that of a circular rod (Figure 2). However, in this invention fiber morphology can be varied from round spaghetti-like, to porous (Figure 3), to flat ribbon-like fibers (Figure 4) without varying the conditions of the ES process, namely the bias lent by selecting appropriate emulsion compositions. SEM analyses of the fibers reveal that the transition from round to porous fibers occurs in the range of 2-5% volume fraction of aqueous phase in the emulsion. Above 5% volume fraction of aqueous phase, fibers with a flat-ribbon morphology are obtained. This transition may be explained as follows. At lower aqueous phase volume fractions, the emulsion droplets are relatively stable and there is no further segregation for the entire duration of the ES process. As the emulsion solution is propelled towards the target the polymer fraction, which constitutes the vast majority undergoes solidification due to the evaporation of the volatile organic phase (chloroform) and the resulting fiber stretches as it approaches the target, while the aqueous phase remains entrapped within the rapidly solidifying polymer (oil) phase. The aqueous droplets become regions of instability toward the later stage of solidification as it constitutes a larger portion of the liquid phase, and a surface tension driven phase segregation process can result yielding porous fibers upon the evaporation of the aqueous component. At still higher volume fractions of aqueous phase, the stability of the emulsion is rather poor even at the early stage of ES and solidification and this leads to rapid phase segregation and the encapsulation of larger water droplets within the solidifying polymer phase. As the polymer skin evolves, the aqueous phase coalesce to yield a structure similar to a water filled balloon or a garden hose. The polymer skin eventually collapses, probably after partial evaporation of the entrapped aqueous phase, because of buckling instability in bending a thin wall tube. This yields fibers with flat, ribbon-like morphologies. This mechanism has also been verified through indirect observations in systems containing silica colloids.

While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.